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Sediment Characteristics Affecting Desorption Kinetics of Select PAH and PCB Congeners for Seven Laboratory Spiked Sediments

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Measures of desorption are currently considered important as potential surrogates for bioaccumulation as measures of the bioavailability of sediment-sorbed contaminants. This study determined desorption rates of four laboratory spiked compounds, benzo[*a*]pyrene (BaP), 2,4,5,2′,4′,5′-hexachlorobiphenyl (HCBP), 3,4,3′,4′-tetrachlorobiphenyl (TCBP), and pyrene (PY), to evaluate the effect of sediment characteristics. The compounds were sorbed onto seven sediments with a broad range of characteristics. Desorption was measured by Tenax-TA extraction from aqueous sediment suspensions. Desorption rates were modeled using an empirical three compartment model describing operationally defined rapid, slow, and very slow compartments. The sediments were characterized for plant pigments, organic carbon (OC), total nitrogen (TN), lipids, NaOH extractable residue, lignin, amino acids, soot carbon, and particle size fractions. Desorption from the rapid compartment for each of the planar compounds BaP, PY, and TCBP was significantly correlated to sediment characteristics that could be considered to represent younger (i.e., less diagenetically altered) organic matter, e.g., plant pigment, lipid, and lignin contents. However, for these compounds there were no significant correlations between desorption and OC, TN, soot carbon, or amino acid contents. HCBP desorption was different from the three planar molecules. For HCBP, the flux from the rapid compartment was negatively correlated ($0.1 > p > 0.05$) with the OC content of the sediment. Overall, HCBP desorption was dominated by the amount of OC and the particle size distribution of the sediments, while desorption of the planar compounds was dominated more by the compositional aspects of the organic matter.

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Introduction

Sediment characteristics, such as the amount of organic carbon (OC) (*1*) and the geochemistry of organic matter (*2*), are known to affect the bioavailability of sediment-associated contaminants to sediment-dwelling organisms. Recent research has demonstrated that within a single sediment type, the rapidly desorbed fractions of sediment-associated contaminants correlate with the bioavailable fraction for various environmentally resident and laboratory-spiked PAH (*3*). This confirms earlier modeling efforts suggesting that desorption rate from sediment was critical for the bioaccumulation of sediment-associated contaminants (*4*). Thus, it appears that differences in bioavailability across sediments may be explained by the ability of contaminants to desorb from sediments.

The rate of desorption depends not only on the quantity of organic matter but also on the quality of organic matter. For example, the decrease in the oxygen to carbon (O/C) ratio in soil organic material was directly related to increased phenanthrene binding and hysteresis decreasing its desorption rate (*5*). O/C ratios are indicative of changes in the polarity of organic matter as a function of diagenesis. Therefore, older, more diagenetically processed organic matter apparently binds certain organic contaminants to a greater degree. Similarly, a recent study examining the distribution of PAH in two weathered sediments demonstrated that PAH were preferentially associated with the lower density fraction of sediments containing detrital plant rather than soot carbon (*6*). Moreover, in that study, two conclusions were apparent: (1) PAH partitioning was much greater than predicted by equilibrium partitioning and (2) while the PAH desorption rate was slower from the low-density material, the mass desorbed was greater than from the high-density material (*6*). This latter conclusion resulted from the larger amount of PAH associated with the low-density material (*6*). Further evidence that particle geochemistry affects PAH bioavailability is that coal-derived particles have a greater PAH binding capacity and slower PAH desorption rates than silt/clay particles in sediment (*7*).

A method using TENAX resin extraction as an infinite sink was developed allowing estimation of the maximum desorption rates (*8*) and the size of the operationally defined contaminant compartments (fractions) within a sediment that correspond to fast, slow, and very slow desorption (*9*). Our objective was to quantify organic contaminant desorption of two PAH and PCB congeners as a function of sediment characteristics primarily pertaining to sedimentary organic matter.

Materials and Methods

Compounds. Experiments used a suite of radiolabeled hydrophobic organic contaminants. Two radiolabeled PCB congeners, ^{14}C-2,4,5,2′,4′,5′-hexachlorobiphenyl (HCBP, specific activity 12.6 mCi/mmole) and ^{14}C-3,4,3′,4′-tetrachlorobiphenyl (TCBP, specific activity 12.5 mCi/mmole), were obtained from Sigma Chemical Co. (St. Louis, MO). ^{3}H-benzo[*a*]pyrene (BaP, specific activity 50.0 Ci/mmole) was obtained from Amersham (Arlington Heights, IL), and ^{3}H-pyrene (PY, specific activity 25.2 Ci/mmole) was obtained from Chemsyn Science Laboratories (Lenexa, KS). The radiopurity of the compounds was determined using thin-layer chromatography (TLC) in hexane:benzene (8:2, v:v) and liquid scintillation counting (LSC) (*10*). If needed, the stock was purified using TLC, so the radiopurity of each compound was >98%

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TABLE 1. Coordinates for the Sediment Sampling Locations

Lake Michigan	43°01′48″ N	86°22′12″ W
Lake Huron stn #9	43°38′00″ N	82°13′00″ W
Lake Huron stn #54	45°31′00″ N	83°25′00″ W
West Bearskin Lake, Duluth, MN	48°03′56″ N	90°25′38″ W
Terwilligers Pond, Put-In-Bay, OH	41°39′24″ N	82°49′39″ W
Lake Erie	41°39′48″ N	82°49′46″ W
pond 5, Columbia, MO	39°00′00″ N	92°15′00″ W

prior to use in the experiments. Nonlabeled PY (purity >99%) and BaP (purity >98%) were obtained from Aldrich (Milwaukee, WI).

Sediment Collection. The sediments were obtained from a variety of geographical locations (Table 1) to represent a wide range of sediment characteristics including OC quantity and quality and sediment particle size. Grab sampling was used to obtain the sediments, thus each sample represents the top 5−20 cm of sediment depending on the consolidation of the sediment. The sediments were shipped wet to the laboratory in polyethylene buckets and held at 4 °C until use. All sediments were press sieved through a 1 mm sieve to remove large debris.

Sediment Spiking. Each sediment was spiked with each of two pairs of radiolabeled compounds, ^{14}C-labeled HCBP and ^{3}H-labeled and nonlabeled BaP and ^{14}C-labeled TCBP and ^{3}H-labeled and nonlabeled PY at 360 nmol kg^{-1} for each compound. Equimolar concentrations of each compound were used to ensure that concentration effects would not confound the results. The measured concentrations based on the specific activities of the compound averaged 0.39 ± 0.03 nmol g^{-1} for BaP, 0.37 ± 0.03 nmol g^{-1} for HCBP, 0.34 ± 02 nmol g^{-1} for PY, and 0.35 ± 0.02 nmol g^{-1} for TCBP. For spiking, the rolling jar method (*11*) with a slight modification (*12*) was used. The sediments were rolled at room temperature for 4 h, stored overnight at 4 °C, and rolled for an additional 4 h at room temperature. The sediments were subsequently stored for 7 and 60 d at 4 °C for the BaP/HCBP and 110 days for the PY/TCBP. The combination of 7 and 60 d storage for BaP/HCBP was to examine the impact of aging, while the 110 d storage of PY/TCBP compared to the 60 d storage for BaP/HCBP resulted from operational logistics. The longer equilibration time for the PY/TCBP was expected to have little impact based on previous aging studies with BaP (*13*).

Desorption Rate Determinations. After storage, sediments (100−150 mg wet weight) from each jar were placed in scintillation cocktail (3a70B, RPI International, Mount Prospect, IL), sonicated for 60 s (Tekmar Model TM375 Sonic Disruptor, Cincinnati, OH), and allowed to stand overnight prior to counting. The samples were counted on a Packard Tri Carb model TR2500 scintillation counter (Packard Instruments, Meriden, CT) operated in the dual label counting mode. The samples were corrected for quench using the external standards ratio method after subtracting background. Compound desorption from sediment particles was measured in duplicate using Tenax-TA beads (mesh size 60−80; Scientific Instrument Services, Inc., Ringoes, NJ) as an absorbent in sediment−water suspension (*9*, *14*). The method was slightly modified: 2.3−3.7 g fresh sediment was mixed in 50 mL glass tubes with 48 mL of filtered (Gelman Sciences, glass fiber, type A/E, 1 μm) Huron River water (collected Hudson Mills Metro Park, Dexter, MI) and 0.2 g of Tenax-TA resin. Huron River water has water quality characteristics of pH 8.1−8.3, alkalinity 170−250 mg L^{-1} as $CaCO_3$, and hardness 165−250 mg L^{-1} as $CaCO_3$ (*15*). The dissolved OC in Huron River water has low binding capacity for hydrophobic compounds (*15*) and thus should not be a significant competitor for desorbed contaminant compared to the Tenax-TA resin (*16*). The Tenax-TA resin was replaced 13 times (BaP + HCBP) or 11 times (PY + TCBP) during the 38-d experiment. The resin was removed from the tube by allowing the resin to float to the top and lifting the material out with small-coiled metal strainer. The recovered resin was extracted once with 5 mL of acetone and twice with 5 mL of hexane. Solvents were combined and evaporated to 1 mL, 10 mL of scintillation cocktail was added, and samples were counted for ^{3}H and ^{14}C activity.

Characterization of Sediments. Sediment subsamples (3−6 g wet weight) were taken for dry weight (70 °C, 24 h). Dried sediment samples (0.3 g) were further treated with 1 N HCl (2 mL) and agitated for 24 h to remove carbonates and subsequently dried at 70 °C. A subsample was taken and weighed, and OC and total nitrogen (TN) were determined on a CE Instruments EA 1110 CHN analyzer (ThermoQuest Italia, Milan, Italy). The particle size distribution of the sediments was determined by wet sieving through sieves with 420, 105, 63, 37, and 20 μm mesh. The dry weight, concentration of the model compounds, and OC for each particle size fraction was determined as above for whole sediment. The sediment OC content was measured in triplicate, and sediment particle size distribution was determined in duplicate for all treatments. The sediment soot carbon content was measured using the method described by Gustafsson et al. (*17*).

Total amino acids (TAA) and enzymatically hydrolyzable amino acids (EHAA) as well as sediment phytopigment, lignin, and lipid content were analyzed on freeze-dried sediment samples. EHAA, representing the amount of amino acids readily available to sediment deposit-feeders, were analyzed by incubating 100 mg of dry sediment with proteolytic enzymes (Proteinase-K, Sigma Chemical Co, St. Louis, MO) in a shaking incubator in the dark at 37 °C for 6 h, followed by precipitation of the nondigested proteins with trichloroacetic acid. The supernatant containing digested peptides and amino acids was then further acid hydrolyzed (6 N HCl) under N_2 for 24 h at 110 °C. The samples were then neutralized with pH 8 boric acid buffer, reacted with o-phthaldehyde (OPA), and fluorescence measured (*18*). TAA concentration was analyzed by acid hydrolysis (6 N HCl) of 50 g of dry sediment for 24 h followed by neutralization, reaction with OPA, and fluorescence measurement. All samples were extracted in triplicate. Fluorescence was determined with an excitation wavelength of 340 nm and emission wavelength of 455 nm. EHAA samples were blank corrected using a protease blank. Amino acid concentrations were determined based on an amino acid standard (Sigma AA-S-18) diluted to 0.5, 1.0, 2.5, and 5.0 nmol mL^{-1}.

For plant pigment analysis, freeze-dried sediment samples (four replicates, 10−150 mg each depending on the OC content) were extracted in the dark with 7 mL of ethanol for 20 h at 21 °C (*19*) mixing four times during the extraction. After extraction, samples were centrifuged for 30 min (1500*g*), and 5 mL of ethanol was transferred into the fluorometer cuvette. Fluorescence was measured with a Turner Designs Fluorometer (Sunnyvale, CA). After the initial reading, 2 drops of 10 N HCl were added to the cuvette, the sample was mixed, and a second reading was recorded. The acidification was done to transform all active chlorophyll into phaeopigments. Calculations were made according to Strickland and Parsons (*20*).

Lipid-like compounds were extracted from freeze-dried sediment samples (250−500 mg) by sonicating the samples in 4 mL of chloroform methanol (2:1) for 1 min and allowed to sit for 20 h in the dark at room temperature. Samples were centrifuged, and the solvent was carefully removed by pipet, placed in a clean test tube, and analyzed by spectrophotometric analysis using the method of Van Handel (*21*).

Lignin-phenols were extracted according to the method of Hedges and Ertel (*22*). Sediments were placed in Monel minibombs with 7 mL of 2 N NaOH, 1 g of CuO, and 50 mg of Fe $(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a N_2-filled glovebox. The reaction product (lignin oxidation product − LOP) from each sample was spiked with 100 μL of ethylvanillin (1 mg mL^{-1} in 0.1 N NaOH) as an internal standard and then acidified to pH 1 prior to extraction with ethyl ether. The ether was freshly distilled over an aqueous solution of Nanopure water and $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. After shaking the sample with the freshly distilled ether in a separatory funnel, the organic layer was isolated. Organic extracts were filtered over anhydrous Na_2SO_4 and then concentrated to a thin film in glass tubes. Samples were stored at −20 °C prior to being derivatized and injected on a gas chromatograph. LOPs in the residual extract were analyzed as trimethylsilyl derivatives (BSTFA reagent, Regis Technologies, Morton Grove, IL, U.S.A.) by adding 50 μL of a pyridine:BSTFA (1:1 − v:v) solution. LOPs were analyzed using a Hewlett-Packard 6890 series gas chromatograph/mass spectrometric detector (GC/MS) in the selective ion monitoring mode with a 30 m × 0.25 mm i.d. × 1 μm film thickness DB-5MS capillary column. The GC/MS conditions for sample analysis were as follows: injector and detector temperatures, 300 °C; split injection (1/50) with 1.5 cm^3 min^{-1} of ultrahigh purity He as the carrier gas; initial column temperature 100 °C increased to 270 °C at 4 °C min^{-1} followed by a 16 min isothermal hold. Gas chromatograph response was generally linear over a range of concentrations for each LOP in a mixed LOP standard. A one-point calibration curve of the mixed LOP standard was used daily to confirm retention times, mass spectra, and response factors for each target LOP. The sum of six lignin-phenol monomers (acetovanillone, vanillic acid, vanillin, acetosyringone, syringic acid, syringaldehyde) are referred to as the term ΣLignin and are indicative of the relative contribution of terrigenous organic matter within a natural sample (*22*).

To determine the humic acid content, wet sediment samples (4 g) were extracted with 40 mL of 0.5 M NaOH for 20 h on a shaker. After extraction, samples were centrifuged (5000*g*) for 15 min, and supernatant was neutralized (pH 7) with 10 M HCl. After adjusting the pH, samples were centrifuged again (5000*g*) for 30 min. After the second centrifugation, supernatants were characterized for OC (Shimadzu TOC-5000, Columbia, MD), and the UV−vis spectra were recorded (Perkin-Elmer Lambda 6, Norwalk, CT). From the UV−vis spectra, the absorptivity at 270 nm (ABS_{270} = 1000 × absorbance at 270 nm/OC), the ratio of the absorbance at 250 and 365 nm (E_2/E_3), and the ratio of the absorbance at 465 and 665 nm (E_4/E_6) were calculated to describe the characteristics of the NaOH extractable organic material (*23*).

Modeling Desorption. It is not possible to know absolutely how many compartments and rate constants actually exist for sediment-sorbed compounds. However, it is possible to select models aggregating the compartments into operationally defined compartments (fractions) that appear to have the same rate constant. Selecting the number of compartments is a balance between the amount of data available and the ability of the model to fit the data. In our case, we examined the available data with both two and three compartment empirical models. While both models could fit the data well with a coefficient of determination (COD) > 0.9, the three compartment model always fits the data with a COD > 0.99. The two compartment model could only fit some of the sediments with COD in the range of 0.96−0.97 and was particularly poor at fitting desorption of PY (Supporting Information Figure A1) and the residuals showed substantial bias (Supporting Information Figure A2), whereas the three compartment model fit the data well (Supporting Information Figures A1 and A2). Thus, for consistency, all data were modeled using the triphasic kinetic model assuming no significant readsorption (*9*):

$$S_t/S_0 = F_{\text{rapid}}(e^{-k_{\text{rapid}}*t}) + F_{\text{slow}}(e^{-k_{\text{slow}}*t}) + F_{\text{veryslow}}(e^{-k_{\text{veryslow}}*t})$$

where S_t is the sediment-sorbed amount at time t, S_0 is a sediment-sorbed amount at the start, F is the fraction of a chemical in rapid, slow, and very slow sediment compartment, k is a desorption rate coefficient for respective compartments (h^{-1}), and t is time (h).

The model was fit to the data by nonlinear curve fitting using Scientist, Version 2.01 (MicroMath, St. Louis, MO). At the end of the experiment, replicate tubes were centrifuged (3000*g*), and water (5 mL) and sediment (100 mg wet weight) were taken from each tube, processed as described above, and analyzed for radioactivity. Mass balance was determined by comparing the total amount of compound desorbed plus that remaining in the sediment−water suspension to the initial amount in the sample and was found to vary between 86 and 110%.

Data Analysis. The experimental design produced a large number of variables to address the factors that may be controlling contaminant desorption behavior from sediment. It is clear that many of the measures could covary, and the number of sediments is relatively small, thus the use of multiple variable correlation would not be appropriate. Correlation analysis was performed using SPSS 10.1 for Windows (SPSS Inc., Chicago, IL), and all possible relationships between sediment characteristics and desorption measures were investigated with individual components. While all possible correlations were performed, only correlation coefficients for those that are significant ($p \leq 0.05$) are provided in the tables as part of the Supporting Information.

Results and Discussion

Characteristics of Sediments. The sediments exhibited a wide range of biogeochemical characteristics (Table 2). Linear correlation analyses of the sediment characteristics showed some significant relationships (Supporting Information Table A1). The OC only correlates with TN, TAA, EHAA, and soot carbon. Both the amount of NaOH extractable OC and the amount of EHAA correlated with the amount of soot carbon. There is no clear mechanistic reason biologically derived material as represented by NaOH extractable OC and EHAA should correlate with soot carbon and they likely only represent a covariation with OC. Neither OC, TN, nor soot carbon correlated with the more recent biologically derived fractions of organic matter: pigment, lignin, and lipid components. Moreover, the NaOH extractable portions of the organic matter, which is usually comprised of the operationally defined refractory humic substances (i.e., humic and fulvic acids), were generally inversely correlated with the pigment and lignin portions of the sediment. The lignin, pigment, and lipid measures were generally strongly related. One interpretation of these observations taken together is that the concentration of plant-derived materials in sediments that have not undergone extensive diagenesis intercorrelate. What also shows (Supporting Information Table A1) is that for the larger particle size fractions, these plant-derived materials are most strongly associated with the OC. The TAA in the sediment did not correlate with any of the pigment, lignin, or lipid measures, while the EHAA correlated with some of the measures. Nor was there a strong correlation between TAA and EHAA ($p = 0.07$).

The absorptivity of the NaOH extracted organic matter (ABS_{270}), E_2/E_3 ratio, and E_4/E_6 ratio varied in the sample series from 9 to 46, 3.3 to 4.6, and 3.0 to 5.4, respectively

TABLE 2. Sediment Characteristics[a]

	OC %dw	TN %dw	sootC %dw	NaOH extr. OC %dw	E_4/E_6[b]	pigments (μg/g dw)	TAA[c] (μmol/gdw)	EHAA[d] (μmol/gdw)	ΣLignin[e] (mg/gdw)	lipids (μg/g dw)	E_2/E_3[f]	ABS_{270}[g]
L. Michigan	0.41	0.05	0.03	0.08	5.36	1.6	122.3	17.6	0.067	8.6	4.63	12.09
	(0.01)	(0.004)	(0.01)	(0.01)	(0.39)	(0.12)	(8.9)	(5.4)	(0.006)	(3.5)	(0.2)	(0.39)
L. Huron stn #9	3.71	0.47	0.27	0.81	3.60	5.0	547.4	68.2	0.098	17.9	4.18	9.47
	(0.15)	(0.031)	(0.01)	(0.14)	(0.23)	(0.16)	(118.2)	(10.8)	(0.028)	(5.2)	(0.08)	(0.94)
L. Huron stn #54	3.18	0.39	0.32	0.83	3.99	6.3	319.3	91.4	0.059	20.4	3.82	12.93
	(0.05)	(0.011)	(0.01)	(0.19)	(0.54)	(0.18)	(42.2)	(15.4)	(0.002)	(4.7)	(0.09)	(2.8)
West Bearskin L.	1.25	0.13	0.05	0.26	3.04	5.1	170.0	26.9	0.404	10.0	3.26	25.95
	(0.26)	(0.029)	(0.01)	(0.02)	(0.2)	(0.17)	(18.4)	(3.2)	(0.07)	(2.3)	(0.06)	(1.7)
Terwilligers Pond	4.11	0.48	0.25	0.37	3.34	50.5	547.8	136.9	2.256	53.5	3.34	45.77
	(0.37)	(0.043)	(0.02)	(0.07)	(0.25)	(1.6)	(90)	(9.5)	(0.61)	(0.14)	(0.06)	(5.1)
L. Erie	1.82	0.25	0.16	0.34	4.99	29.5	158.8	73.6	0.088	40.5	4.04	19.02
	(0.05)	(0.022)	(0.01)	(0.02)	(0.28)	(0.18)	(97.8)	(1.0)	(0.05)	(10.4)	(0.19)	(1.2)
pond 5	3.00	0.29	0.16	0.45	4.26	42.8	426.9	75.4	1.425	49.9	3.93	23.32
	(0.27)	(0.065)	(0.01)	(0.13)	(0.48)	(2.6)	(33.4)	(4.9)	(0.90)	(7.5)	(0.05)	(4.2)

[a] The numbers in parentheses are standard deviation ($n = 3$). [b] E_4/E_6 = the ratio of the absorbance at 465 nm divided by the absorbance at 665 nm (measured in NaOH extract of sediment). [c] TAA = total amino acids. [d] EHAA = enzymatically hydrolyzable amino acids. [e] ΣLignin = lignin derived phenols in sediment. [f] E_2/E_3 = the ratio of the absorbance at 250 nm divided by the absorbance at 365 nm (measured in the NaOH extract of sediment). [g] ABS_{270} = 1000 × (absorbance at 270 nm)/OC in the NaOH extract of sediment.

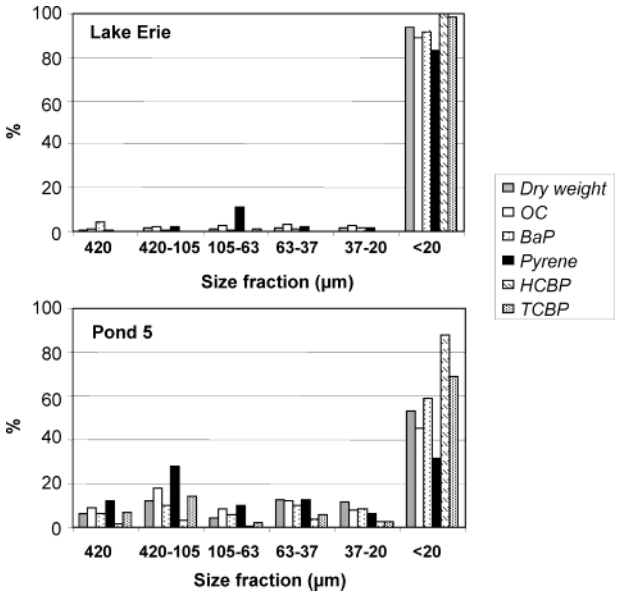

FIGURE 1. Percent particle size distribution, OC, BaP, pyrene, HCBP, and TCBP in two sediments. These two sediments are examples of the extremes in distribution patterns, and the other five sediments exhibit distributions between these two.

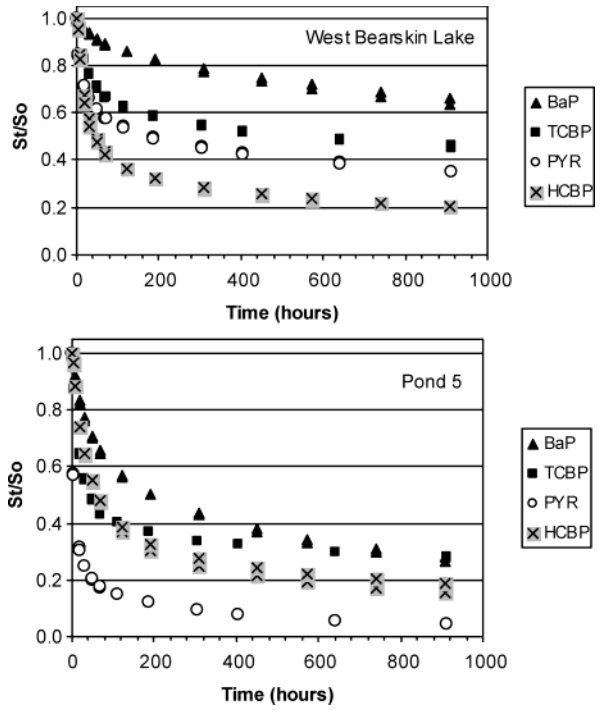

FIGURE 2. Desorption of model compounds, shown as the fraction of contaminant remaining in sediment over time, from West Bearskin Lake and pond 5 sediment. These two sediments illustrate the differences in desorption characteristics found among the sediments.

(Table 2). According to Chen et al. (*24*), a high E_4/E_6 ratio is proportional to the degree of humification and inversely related to the molecular weight of the humic substances as measured by the colligative properties of material extracted from soil. Schnitzer (*23*) found that the E_4/E_6 values for humic acids and fulvic acids extracted from soils are within the range of 3.8−5.8 and 7.6−11.5, respectively. Further, fulvic acids from strongly humic and oligotrophic waters are characterized by an E_2/E_3 ratio of about four (*25*). The absorptivity of the sample at 270 nm (ABS_{270}) reflects the absorbance of $\pi-\pi$ transitions in substituted benzene rings and most polyenes and has been related to the aromatic content of isolated soil humic acids (*26, 27*). Based on these descriptions, the NaOH extractable organic matter in West Bearskin Lake and Terwilligers Pond sediments has the most aromatic character (ABS_{270}: 26−46) and the highest molecular weight (E_4/E_6: 3−3.3). However, this NaOH extractable organic matter fraction represents only 9.1% of the OC in Terwilligers Pond sediment but represents 21.1% in West Bearskin Lake sediment. These two sediments also contained the greatest concentration of lignin-derived phenols (Table 2).

Although the majority of each compound was generally associated with the <20 μm size particles, there were differences in the distribution of the contaminants among the particle size classes between the sediments (e.g. Figure 1). Further, these differences in distribution did not completely correlate with the amount of OC in the size fraction. This is consistent with previous studies examining the relationship of contaminant and OC distribution in sediments (*2, 13*). These results continue to support the hypothesis that OC quality as well as quantity is important for contaminant binding. Moreover, this compositional dependence varies across each size class of natural particles.

Desorption among Sediments and between Compounds. Desorption rates and compartment size differed substantially among the compounds and sediments as illustrated in Figure 2 (Tables 3 and 4, Figures 3 and 4, Supporting Information

TABLE 3. Desorption Rate Constants (h^{-1}) for the Rapid, Slow, and Very Slow Compartments of Spiked BaP and HCBP after 7 and 60 days Contact Time[a]

	7 days			60 days		
	Krap	Kslow	Kvslow	Krap	Kslow	Kvslow
			BaP			
L. Michigan	0.065	0.0092	0.00033	0.069	0.0104	0.00061
	(0.014)	(0.0021)	(0.00008)	(0.008)	(0.0016)	(0.00003)
L. Huron 9	0.048	0.0057	0.00025	0.030	0.005	0.00036
	(0.016)	(0.0011)	(0.00005)	(0.038)	(0.008)	(0.0002)
L. Huron 54	0.048	0.0070	0.00049	0.0257	0.0057	0.00039
	(0.010)	(0.0014)	(0.00013)	(0.009)	(0.0041)	(0.00012)
W. Bearskin L.	0.0322	0.0037	0.00012	0.0259	0.0029	0.00021
	(0.010)	(0.0025)	(0.00015)	(0.010)	(0.0045)	(0.0021)
Terwilligers P.	0.048	0.0061	0.00024	0.0312	0.0049	0.00037
	(0.005)	(0.0010)	(0.00008)	(0.012)	(0.0042)	(0.00029)
L. Erie	0.0459	0.0087	0.00069	0.0318	0.0051	0.00050
	(0.012)	(0.0020)	(0.00012)	(0.0064)	(0.0033)	(0.00027)
Pond 5	0.0448	0.0076	0.00039	0.0343	0.0059	0.00060
	0.0123)	(0.0028)	(0.00015)	(0.0039)	(0.0015)	(0.00010)
			HCBP			
L. Michigan	0.137	0.0186	0.00039	0.159	0.0184	0.00054
	(0.027)	(0.0073)	(0.00012)	(0.018)	(0.0041)	(0.00006)
L. Huron 9	0.068	0.0121	0.00046	0.055	0.0108	0.00063
	(0.009)	(0.0042)	(0.00013)	(0.009)	(0.0056)	(0.00017)
L. Huron 54	0.127	0.0270	0.00132	0.060	0.0100	0.00041
	(0.028)	(0.0047)	(0.00014)	(0.012)	(0.0069)	(0.00019)
W. Bearskin L.	0.056	0.0115	0.00050	0.050	0.0092	0.00047
	(0.005)	(0.0024)	(0.00009)	(0.004)	(0.0026)	(0.00009)
Terwilligers P.	0.041	0.0091	0.00029	0.033	0.0071	0.00029
	(0.009)	(0.0051)	(0.00017)	(0.005)	(0.0036)	(0.00013)
L. Erie	0.052	0.0136	0.00088	0.0468	0.0070	0.00041
	(0.005)	(0.0034)	(0.00013)	(0.0045)	(0.0052)	(0.00029)
Pond 5	0.038	0.0084	0.00032	0.032	0.0079	0.00056
	(0.006)	(0.0084)	(0.00018)	(0.006)	(0.0039)	(0.00020)

[a] The numbers in parentheses represent the standard error from the regression.

TABLE 4. Desorption Rate Constants (h^{-1}) for the Rapidly, Slowly, and Very Slowly Compartments of Spiked Pyrene and TCBP after 110 Days Contact Time[a]

	pyrene			TCBP		
	Krap	Kslow	Kvslow	Krap	Kslow	Kvslow
L. Michigan	0.317	0.0174	0.00063	0.166	0.0163	0.00036
	(0.036)	(0.0029)	(0.00007)	(0.017)	(0.0016)	(0.00003)
L. Huron 9	0.153	0.0122	0.00049	0.059	0.0077	0.00029
	(0.026)	0.0018)	(0.00005)	(0.008)	(0.0022)	(0.00005)
L. Huron 54	0.278	0.0238	0.00099	0.083	0.0157	0.00046
	(0.034)	(0.004)	(0.00008)	(0.017)	(0.0038)	0.00005)
W. Bearskin L.	0.222	0.0166	0.00045	0.046	0.0063	0.00021
	(0.021)	(0.0016)	(0.00003)	(0.004)	(0.0018)	(0.00005)
Terwilligers P.	0.232	0.0246	0.00119	0.064	0.0103	0.00030
	(0.034)	(0.0065)	(0.00023)	(0.011)	(0.0055)	(0.00012)
L. Erie	0.304	0.0222	0.00071	0.136	0.0153	0.00060
	(0.080)	(0.0093)	(0.00023)	(0.026)	(0.0037)	(0.00010)
pond 5	0.316	0.0412	0.00183	0.069	0.0109	0.00027
	(0.021)	(0.0055)	(0.00015)	(0.004)	(0.0024)	(0.00005)

[a] The numbers in parentheses represent the standard error from the regression.

Figures A3−A6 and Tables A3 and A4). Compound equilibrium in the sediments can be evaluated for each operationally defined compartment. Using five half-lives to represent time to equilibrium (97%), then the time for each compartment to reach equilibrium can be evaluated. Using the slowest desorption measure among the sediments for each compound, the rapidly desorbed compound would require a range of 23 h (PY) to 134 h (BaP) to reach equilibrium. Thus, even at the shortest storage time, 7 d, this compartment would be at equilibrium. For the slow compartment, the range was 284 h (PY) to 1195 h (BaP), thus this compartment is at equilibrium in less than 60 d. The very slow compartment is generally not at equilibrium with the half-life ranging from 1414 h (PY) to 5775 h (BaP). It may be that equilibrium in this compartment is never reached even in the field within the biologically active sediments as many conditions could change in the 0.8−3.3 y required for equilibrium within such an active layer.

Desorption rates (k_{rap} and k_{slow}) for BaP were generally slower in most sediments than for HCBP (Table 3). The main exception was for the pond 5 sediment where desorption rates were similar for both compounds. The desorption rate was not correlated with the amount of OC in the sediment (Tables 1 and 3). The slowest desorption rate was from the West Bearskin Lake sediment, and the most rapid desorption rate was from the Lake Michigan sediment. Desorption rate

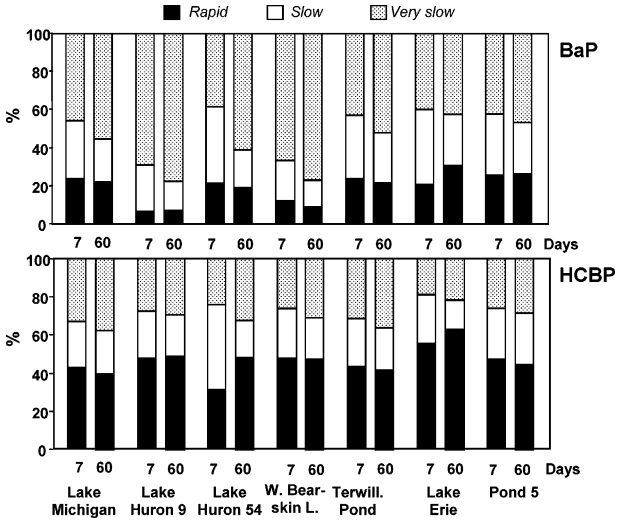

FIGURE 3. The distribution of the rapidly, slowly, and very slowly desorbing compartments (fractions) of spiked BaP and HCBP in different sediments after 7 and 60 days contact time. The average coefficients of variation for the HCBP fractions are 14.4, 24.6, and 20.9% (60 d) and 16.7, 22.8, and 8.5% (7 d) for the rapid, slow, and very slow compartments, respectively, while for BaP the coefficients of variation are 44.7, 39.9, and 16.9% (60 d) and 21.2, 23.4, and 8.9% (7 d) for the rapid, slow, and very slow compartments, respectively.

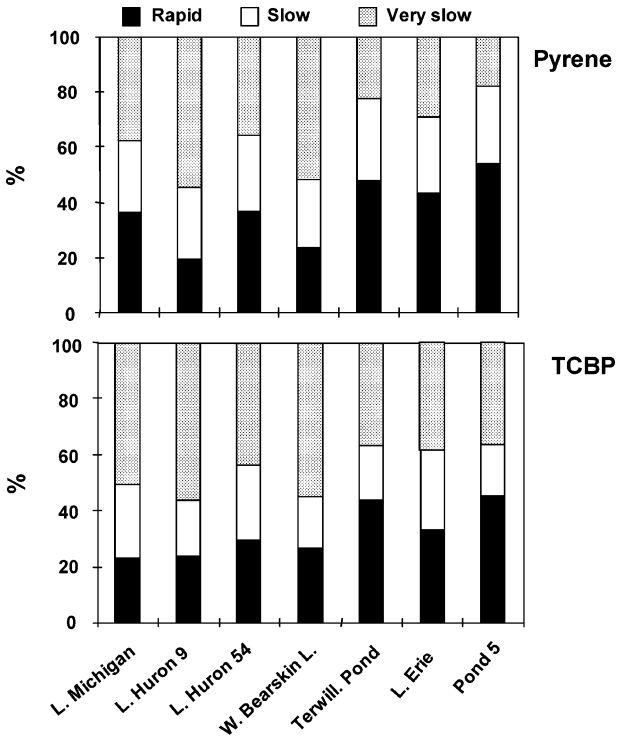

FIGURE 4. Distribution of the rapidly, slowly, and very slowly desorbing compartments (fractions) of spiked pyrene and TCBP in different sediments after 110 days contact time. The average coefficients for variation for the pyrene fractions are 8.3, 9.8, and 7.3% for the rapid, slow, and very slow compartments, respectively, while for the TCBP fractions the coefficients of variation are 10.6, 13.0, and 6.3%, respectively, for the rapid, slow, and very slow compartments.

constants showed little difference irrespective of equilibration time, 7 and 60 d (Table 3). Thus, each region of the sediment particles that results in the different rates of desorption appears to be readily defined early in the sorptive process. The compartment of rapidly desorbable compound was much smaller for BaP than for HCBP at both storage times (Figure 3, Supporting Information Table A3). However, for both compounds, the amount of compound in the very slowly desorbed compartment tended to increase with increasing equilibration time. Most of the differences in the two equilibration periods (7 and 60 d) were manifested in a reduction of the slowly desorbed compartment moving to the very slowly desorbed compartment for both compounds and especially for BaP (Figure 3). This trend in the movement of compounds toward the very slowly desorbed compartment supports the observations of decreasing bioavailability with increasing equilibration time as has been frequently observed in the literature (e.g., ref *28*). Further, desorption measures do not predict the time course of the aging process. As a result, desorption as a surrogate for bioavailability must be determined each time bioavailability estimates are desired.

Compound desorption was most rapid for PY relative to TCBP in all desorption compartments (Table 4). As with BaP and HCBP, the rate of desorption was not correlated with the amount of OC in the sediment. Distribution of both compounds among desorption compartments for PY and TCBP was intermediate between BaP and that observed for HCBP (Figures 3 and 4). It was surprising that TCBP exhibited smaller rapidly desorbing compartments than HCBP since it is more water-soluble and would therefore be expected to be more desorbable. However, TCBP and PY were equilibrated longer than the BaP and HCBP. Increasing the sorption time for BaP/HCBP had its affect mostly on reducing the slow and increasing the very slowly desorbing compartments and did not appear to affect the rapid compartment. Thus, the difference between TCBP and HCBP is likely more a feature of the planar nature of TCBP than limited changes in equilibrium. The rate constants for desorption of TCBP and HCBP were similar (Tables 3 and 4). Thus, the flux of compound desorbing off sediment particles (desorption rate constant times the amount in the compartment) would be smaller for TCBP than for HCBP due to the smaller rapidly desorbing compartment for TCBP. As a result, the bioavailability is expected to be lower for the TCBP. For PY, the amount in the rapidly desorbed compartment is larger than for BaP and similar to that for TCBP. With the substantially larger rate constants for PY compared to BaP and TCBP, it should be readily desorbed and bioavailable. Generally, in sediment bioavailability studies, PY has been found to be the most bioavailable among the compounds studied (*2*).

Factors That Influence Contaminant Desorption. In general, across all sediments, the two PAH and the coplanar TCBP behaved similarly, while the noncoplanar HCBP behaved differently with respect to the sediment characteristics (Supporting Information Table A2). The factors that produced positive correlations with desorption flux and the size of the rapidly and slowly desorbing compartments of the PAH and TCBP were the pigments and lipids in the sediment (Figures 3 and 4, Supporting Information Table A2). For BaP, the flux from the particles associated with the rapid and slow desorbing compartments was directly influenced by the amount of lipid per amount of OC (Supporting Information Table A2). BaP flux was also positively correlated with the amount of compound associated with the greater than $\geq 420\,\mu$m particle size fraction as well as the E_4/E_6 ratio for the extractable organic matter. The flux of BaP was negatively correlated with the amount of compound found in the NaOH-extractable residue, presumably the amount associated with humic acids. The size of the rapid and slow desorption compartments were directly related to the amount of pigment per amount of OC and the amount of lipid per amount of OC. Thus, factors that indicate the relatively young character of the sediment organic matter increased the size of the compartments that are most likely to contribute to the rapid desorption, which appears to contribute most to the bioavailable fraction (*3*).

For PY desorption, the correlations between desorption and sediment characteristics are not as strong or clear but follow those of BaP (Supporting Information Table A2). This is likely the result of the lower log K_{ow} that leads to lower binding affinity. As with BaP, the size of the compartments was related to the amount of pigments and the amount of pigment per amount of OC. A similar relationship of increasing compartment size for the rapidly and slowly desorbing fractions was observed with the amount of lipids and lipids per OC. These sediment characteristics may be responsible for the trend of increasing flux among the sediments, but the correlations were not quite significant, e.g. $0.1 > p > 0.05$ (Supporting Information Table A2). The size of and flux from the slowly desorbing compartment was positively correlated to the amount of pyrene on the ≥ 420 μm particle fraction. Thus, the quality of the organic matter in the sediment was clearly critical for PY desorption kinetics.

For TCBP, the correlation pattern for desorption characteristics was similar to the PAH particularly with the role of lipid and lipids per amount of OC increasing desorption flux from the sediment (Supporting Information Table A2). The size of the rapidly desorbing compartment increased with the amount of pigment per amount of OC and amount of lipids. The size of the slowly desorbing compartment was positively correlated to the amount of lipid per amount of OC, as was the flux from the rapidly desorbing compartment.

The size of the very slowly desorbing compartment was correlated to the amount of NaOH-extractable OC for BaP and to the amount of OC in the 63−37 μm particle size fraction for TCBP (Supporting Information Table A2). Other than these two correlations, there were no positive correlations for the very slow compartment with these three compounds (BaP, PY, and TCBP). There were negative correlations between the sediment characteristics and the compartment size for these three compounds, but these are essentially the inverse correlates to the rapid compartment. The rate constant for desorption for the very slow compartment like that of the other two compartments was positively correlated to the E_4/E_6 ratio for BaP (Supporting Information Table A2). If one follows the soft (amorphous) versus hard (condensed) carbon model to describe desorption (*29*), then the pigments, lignin, and lipid that control the rapidly desorbing compound may be equivalent to the soft carbon, and the humics, fulvics, and soot carbon may be considered the hard carbon based on the factors that appear to control desorption kinetics of BaP, PY, and TCBP.

HCBP did not behave like the more planar compounds (Supporting Information Table A2). Fewer significant correlations were found because the rates were not very different among the sediments (Table 3). HCBP was the only compound to exhibit an interaction with OC, but the negative correlation of desorption rate constant for the rapidly desorbing compartment versus OC was not significant ($p = 0.83$). The flux from the rapidly desorbing compartment and the combination of the rapid and slowly desorbing compartments exhibited weak negative correlations to OC ($0.1 > p > 0.05$). There were significant positive correlations for desorption flux of HCBP that were correlated to the E_2/E_3 ratio and the amount of compound on the 105−63 μm and the 63−37 μm fractions. The E_2/E_3 ratio and the amount of compound on the 105−63 μm fraction gave strong positive correlations to the rate constant for desorption for the rapid and slowly desorbing compartments. According to De Haan (*26*), fulvic acids from strongly humic and oligotrophic waters are characterized by an E_2/E_3 ratio of about four. The values found for the sediments used in this study had ratios near 4 (Table 2). The size of the rapidly desorbing compartment was positively correlated to the amount of HCBP on the <20 μm particle size fraction and the amount of fine (<63 μm) particles. Thus, the major factors controlling desorption of HCBP from sediments seems to be the amount of OC and the distribution of the OC within the sediment which relates more to the particle size than any other sediment characteristic. Clearly, the number of sediments used in this study was limited. However, there appears to be a clear difference in desorption characteristics between the planar compounds and the nonplanar HCBP that could affect bioavailability.

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Supporting Information Available

Details of the correlations among the sediment characteristics and between the sediment characteristics and desorption parameters and the fits to desorption data for all sediments as well as an example of the difference between using a two-phase and three-phase model to fit desorption data. This material is available free of charge via the Internet at http://pubs.acs.org.

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